



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : A61K 7/06		(11) International Publication Number: WO 00/57846	
A1		(43) International Publication Date: 5 October 2000 (05.10.00)	
(21) International Application Number: PCT/EP00/01945 (22) International Filing Date: 6 March 2000 (06.03.00) (30) Priority Data: 60/126,027 25 March 1999 (25.03.99) US 09/307,060 7 May 1999 (07.05.99) US (71) Applicant (for AE AU BB CA CY GB GD GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT TZ UG ZA ZW only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB). (71) Applicant (for all designated States except AE AU BB CA CY GB GD GH GM IE IL IN KE LC LK LS MN MW NZ SD SG SL SZ TT TZ UG ZA ZW): UNILEVER NV [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL). (71) Applicant (for IN only): HINDUSTAN LEVER LIMITED [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Mumbai 400 020, Maharashtra (IN).		(72) Inventors: NEKLUDOFF, Natalia; Unilever Home & Personal Care USA, 3100 East Golf Road, Rolling Meadows, Chicago, IL 60008 (US). DABKOWSKI, Diane, Marie; Unilever Home & Personal Care USA, 3100 East Golf Road, Rolling Meadows, Chicago, IL 60008 (US). VASUDEVAN, Tirucherali, Varahan; Unilever Home & Personal Care USA, 3100 East Golf Road, Rolling Meadows, Chicago, IL 60008 (US). SEPER, Jennifer, Marie; Unilever Home & Personal Care USA, 3100 East Golf Road, Rolling Meadows, Chicago, IL 60008 (US). (74) Agent: GRIFFITHS, Helen, Sarah; Unilever plc, Patent Department, Colworth House, Sharnbrook, Bedford, Bedfordshire MK44 1LQ (GB). (81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(54) Title: LOW VOC HAIR SPRAY COMPOSITIONS HAVING ENHANCED STYLING BENEFITS (57) Abstract An aqueous or hydroalcoholic, aerosol or non-aerosol hair styling aid or mousse composition containing a water soluble or dispersible fixative polymer in an amount from 1 % to 40 % by weight of the composition, a neutralizing agent in an amount from 0.1 to 10 wt.%, a hydrocarbon based surfactant in an amount from 0.01 % to 5 % by weight, a salt from 0.01 % to 10 % by weight, alcohol from 10 % to 90 % by weight, a volatile ester from 0 to 90 % by weight, a volatile ketone from 0 to 90 % by weight and water from 10 % to 98 % by weight of the composition. Additionally, aerosol compositions contain a liquefied propellant gas from 5 % to 60 % by weight of the composition.			

- 1 -

LOW VOC HAIR SPRAY COMPOSITIONS HAVING ENHANCED STYLING
BENEFITS

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BACKGROUND OF THE INVENTION

- 10 Regulations and laws designed to protect the environment, are leading to the production of hair care spray products which have lower volatile organic compounds (VOC) content than the current commercial products.
- 15 This invention relates to 55% VOC (and lower VOC) hair spray compositions that provide hold and feel properties similar to or better than that of the current 80% VOC hair sprays. The performance characteristics of hair sprays suffer as the VOC level is reduced from 80% to 55% in the product.
- 20 Therefore, preparing 55% VOC (and lower VOC) hairspray products which have the same or better performance characteristics as 80% VOC hairspray products would be desirable.
- 25 U.S. patents in this area of technology are as follows:
U.S. Patent 5,374,420 discloses a hairspray/ hair setting composition comprising:
- a) 0.001-20% of a neutralizable hair fixative resin,
 - b) 0.001-8% of a base, and
 - 30 c) 0.001-5% of an acid surfactant precursor in an alcohol or aqueous/alcohol carrier.

- 3 -

wt %, a hydrocarbon based surfactant in an amount from about 0.01% to about 5% by weight, a salt from about 0.01% to about 10% by weight, alcohol from about 0% to about 90%, more preferably, from about 10% to about 90% by weight, a
5 volatile ester from about 0 to 90% by weight, more preferably about 10% to about 90% by weight; a volatile ketone from about 0 to 90% by weight, more preferably about 10% to about 90% by weight; in the case of aerosols from about 5 to about 60% by weight of liquidfied propellant gas,
10 and water from about 10% to about 98% by weight of the composition.

As can be seen the compositions of the invention can be aqueous or hydroalcoholic.

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DETAILED DESCRIPTION OF THE INVENTION

As used herein, % means weight % of the total composition
20 unless otherwise indicated. "m N/m" means milli Newtons/meter. Dynes/cm is the same as milli Newtons/meter.

The starting materials set forth herein are either known or can be prepared according to known methods. The compositions
25 of the invention can be prepared either by known methods or by methods analogous to known methods.

As noted above, in the present invention, the deterioration of the spray characteristics of a hydroalcoholic solution
30 containing the hair spray resin which occurred as the VOC content was reduced from 80 to 55% was offset by

- 5 -

tris(hydroxymethyl)aminomethane, triethanol amine, sodium hydroxide, and potassium hydroxide.

In the present invention, the soluble or dispersible fixative polymer may be selected from the group consisting of: vinyl and acrylic based resins and polyurethane resins. Specific resins include, but are not limited to, acrylamide copolymers, acrylate copolymers, which may or may not be modified by introduction of a quaternary ammonium group.

Other fixative resins are described in copending U.S. Patent Application Serial No. 08/717,113 to Bhatt et al, filed September 20, 1996. The use of resins or polymers in hairsprays is known as summarized in Grollier et al U.S. Patent No. 4,445,521. The molecular weight of the polymer has a preferred range of about 10,000 to about 1 million Daltons, a more preferred range is about 20,000 to about 500,000 Daltons and the most preferred range is about 30,000 to about 300,000.

In the present invention, the inorganic salt may be selected, for example, from the group consisting of chloride, sulfate, and nitrate salts of sodium, magnesium and ammonium.

In the present invention, the alcohol, if present, may be selected from the group consisting of: ethanol and isopropanol.

In the present invention volatile ester, if present, may be selected, for example, from the group methyl acetate, ethyl acetate, propyl acetate, butyl acetate.

- 7 -

about 1% to about 40 % by weight of the composition, a neutralizing agent in an amount from about 0.1 to about 10 wt %, a hydrocarbon based surfactant in an amount from about 0.01% to about 5% by weight, a salt from about 0.01% to about 10% by weight, alcohol from about 0% to about 90%, more preferably 10% to about 90% by weight, a volatile ester from 0 to 90% by weight, more preferably about 10% to about 90% by weight, a volatile ketone from about 0% to about 90%, more preferably, from about 10% to about 90% by weight and water from about 10% to about 98% by weight of the composition. Additionally, in the case of aerosols, a liquefied propellant gas is present from about 5% to 60% by weight.

As can be seen, the compositions of the invention can be aqueous or hydroalcoholic.

Preferred ranges of a water soluble or dispersible fixative polymer are about 1 to about 40% by weight of the composition, more preferably about 2 to about 20%, and most preferably about 3 to about 10%.

Preferred ranges of a neutralizing agent are about 0.1 to about 10% by weight of the composition, more preferably about 0.25% to about 5%, and most preferably about 0.5% to about 2.5%.

Preferred ranges of a hydrocarbon based surfactant are about 0.01% to about 5% by weight of the composition, more preferably about 0.05% to about 2.5%, and most preferably about 0.1% to about 1.0%.

- 9 -

polymer is a methacrylic acid, n-butyl acrylate and ethyl methacrylate copolymer in the molecular weight range about 10 to about 1000 Kilo Daltons, preferably about 20 to 500 Kilo Daltons, and most preferably about 50 to about 300 Kilo Daltons. Also preferred are compositions of the invention in which the polymer is a butyl acrylate, methyl methacrylate, hydroxyethyl methacrylate and methacrylic acid copolymer in the molecular weight range of about 10 to about 1000 Kilo Daltons, preferably about 20 to 500 Kilo Daltons, and most preferably about 50 to about 300 Kilo Daltons. Also preferred are compositions of the invention in which the polymer is a vinyl acetate, crotonates and vinyl neodecanoate copolymer in the molecular weight range of about 10 to about 1000 Kilo Daltons, preferably about 20 to 500 Kilo Daltons, and most preferably about 50 to about 300 Kilo Daltons.

Also preferred are compositions of the invention in which the polymer is a butyl ester of vinyl methyl ether and maleic anhydride copolymer in the molecular weight range about 10 to about 1000 Kilo Daltons, preferably about 20 to 500 Kilo Daltons, and most preferably about 50 to about 300 Kilo Daltons. Also preferred are compositions of the invention in which the polymer is an ethyl ester of vinyl methyl ether and maleic anhydride copolymer in the molecular weight range about 10 to about 1000 Kilo Daltons, preferably about 20 to 500 Kilo Daltons, and most preferably about 50 to about 300 Kilo Daltons. Also preferred are compositions of the invention in which the polymer consists of polystyrene sulfonate monomers in the molecular weight range of about 10 to about 1000 Kilo Daltons, preferably

- 11 -

acid form. Also preferred are compositions of the invention in which the anionic surfactant is magnesium dioctyl sulfosuccinate or its acid form. Also preferred are compositions of the invention in which the anionic
5 surfactant is ammonium dioctyl sulfosuccinate or its acid form. Also preferred are compositions of the invention in which the anionic surfactant is sodium dodecyl sulfate or its acid form. Also preferred are compositions of the invention in which the anionic surfactant is magnesium
10 dodecyl sulfate or its acid form. Also preferred are compositions of the invention in which the anionic surfactant is ammonium dodecyl sulfate or its acid form. Also preferred are compositions of the invention in which the anionic surfactant is sodium laureth sulfate or its acid
15 form.

Also preferred are compositions of the invention in which the anionic surfactant is magnesium laureth sulfate or its acid form. Also preferred are compositions of the invention
20 in which the anionic surfactant is ammonium laureth sulfate or its acid form.

Also preferred are compositions of the invention in which the hydrocarbon based surfactant is a zwitterionic
25 surfactant. Also preferred are compositions of the invention in which the zwitterionic surfactant is cocoamidopropyl betaine.

Also preferred are compositions of the invention in which
30 the salt is an organic salt. Also preferred are compositions of the invention in which the organic salt is sodium

- 13 -

are compositions of the invention in which the neutralizing agent is sodium hydroxide. Also preferred are compositions of the invention in which the neutralizing agent is potassium hydroxide.

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Also preferred are aerosol compositions of the invention in which the liquefied propellant gas is dimethyl ether. Also preferred are aerosol compositions of the invention in which the liquefied propellant gas is a mixture of propane and butane as well as mixtures of dimethyl ether, propane and butane.

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Hair spray compositions of the invention can be in the form of hair sprays, spritzes, mousses etc.

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The invention also relate to a method of treating or styling hair which comprises contacting said hair with the hairspray compositions of the invention. After hair spray compositions are applied to the hair, said hair can be styled, etc in various ways which are known in the art.

20

What follows are non-limiting examples of hair spray compositions of the invention.

The materials, definitions, and performance criteria, for low VOC Compositions of the invention having enhanced styling benefits are set forth just below.

25

Materials

30

Polymers

- 15 -

Hydrocarbon surfactants

Sodium dioctyl sulfo succinate : Monawet MO 75-E from
Uniqema, NJ, USA

5

Sodium dodecyl sulfate : Obtained from BDH Laboratory
supplies, Poole, England

Cocoamidopropyl betaine : Tegobetaine from GoldSchmidt
10 Industries

Sodium laureth sulfate (2 moles EO) : Empicol ESB 3/AQ
from Albright & Wilson, IL, USA

15 Organic salts:

Sodium benzoate : Boric chemical, IL USA

Magnesium acetate : Aldrich, WI, USA
20

Propellant

Dimethyl ether : Dymel DME from DuPont Chemical Co.,
Wilmington, DE USA
25

DefinitionsDynamic Surface Tension

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- 17 -

The difference in surface tension obtained at a surface age of about 10 msec and that obtained at a surface age of about 1500 msec ($\Delta_{10-1500}$) was chosen as the criterion for comparing the performance of different hair spray solutions.

5

An absolute surface tension value at about 11 msec was chosen as a criterion for comparing the performance of different hair spray solutions.

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Preparation of 55% VOC Non-Aerosol and Aerosol Hairspray Solutions

Equipment

15

Fawcett Co, Model 103-A Mixer
Mettler Toledo PG5002-S balance
medium sized stir bar (optional)
beaker

20

transfer pipets
USA Standard Testing Sieve #100, WS Tyler Unc.
150micrometer

Procedure

25

1. Add item#1, SD Alcohol 40-B into a suitably sized container.
2. Begin moderate agitation using an overhead mixer or a stir bar.
- 30 3. Add item#2, neutralizer. Increase agitation to high setting until a vortex is created.

Table 1
55% VOC Non-Aerosol Hair Spray Compositions

Test Solution #	1	2	3	4	5	6	7	8	9	10	11	12
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wt%

Component CONTROL

5

Ethanol	53.0	55.0	55.0	55.0	55.0	55.0	55.0	55.0	55.0	55.0	55.0	55.0
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Isopropanol	2.0	-	-	-	-	-	-	-	-	-	-	-
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2-amino,2-methyl, 1-propanol	0.91	0.82	0.82	0.82	0.82	0.82	0.82	0.82	0.82	0.82	0.82	0.41
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Amphomer 28-4910	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	3.0
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Dimethicone copolyol	-	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
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20 Cyclomethicone	-	0.13	0.13	0.13	-	-	-	-	-	-	-	-
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Table 2
55% VOC Non-Aerosol Hair Spray Compositions

5	Test Solution #	13	14	15	16	17	18	19	20	21	22	23
Component		wt%										
10	Ethanol	55.0	55.0	55.0	55.0	55.0	55.0	55.0	55.0	55.0	55.0	55.0
	2-amino,2-methyl, 1-propanol	0.84	0.84	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.37
	HC 7801	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	3.0
15	Dimethicone copolyol	-	-	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	Cyclomethicone	-	-	0.13	0.13	0.13	0.13	0.13	0.13	-	-	-
20	Sodium dodecyl sulfate	-	-	-	-	-	-	-	0.2	-	-	-

Table 3
55% VOC Aerosol Hair Spray Compositions

Test Solution #	24	25	26	27	28	29	30	31	32	33	34
Component	wt%										
Ethanol	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
2-amino, 2-methyl, 1-propanol	0.56	0.56	0.56	0.56	0.56	0.56	0.56	0.56	0.56	0.56	0.29
Resyn 28-2930	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	3.0
Dimethicone copolyol	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Cyclomethicone	0.13	0.13	0.13	-	-	-	-	-	-	-	-
Sodium dodecyl sulfate	-	-	-	-	-	-	-	0.2	-	-	-

Table 4
55% VOC Aerosol Hair Spray Compositions

Test Solution #	35	36	37	38	39	40	41	42	43	44	45
Component	wt%										
Ethanol	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
2-amino,2-methyl, 10 1-propanol	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.37
Amphomer LV-71	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	1.25
Resyn 28-2930	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	1.25
15 Dimethicone copolyol	-	-	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Cyclomethicone	-	-	0.13	0.13	0.13	0.13	0.13	-	-	-	-
20 Sodium dodecyl sulfate	-	-	-	-	-	-	-	0.2	-	-	-

- 27 -

As used in this specification, test solutions of a certain number refer to the test solutions in the tables just above. Thus, test solution #1 is the first solution in the above table 1 and test solution #16 is the sixteenth solution which appears in table 2.

Example 1

Comparison of Dynamic Surface Tension of 55% VOC Test Hair Spray Solutions with Commercial Hair Sprays

A combination of an organic salt (sodium benzoate) and a hydrocarbon surfactant is required to bring the surface tension difference of the 55% VOC test solution down to that of 80% VOC commercial product. A Test solution in which only a hydrocarbon based surfactant is used, a Test solution in which a combination of silicone and hydrocarbon surfactants is present, or test solutions in which a combination of an organic salt and a silicone based surfactant is present do not bring the surface tension difference to that of the 80% VOC product.

Example 2

Comparison of Sodium Benzoate and Magnesium Acetate

Using the Dynamic Surface Tension measurement described herein (units of measurement are mN/m) it was shown in test solutions (that is, compositions of the invention) that both sodium benzoate and magnesium acetate brings the surface

Example 5Comparison of Sodium Benzoate and Magnesium Acetate

5 Using the Dynamic Surface Tension measurement described
herein (units of measurement are mN/m) it was shown it was
shown in test solutions (that is, compositions of the
invention) that both sodium benzoate and magnesium acetate
bring the surface tension difference of the 55% VOC test
10 solution closer to that of the commercial product , also
with HC 7801 styling resin.

Example 6

15 Effect of Different Surfactants on Dynamic Surface Tension

Using the Dynamic Surface Tension measurement described
herein (units of measurement are mN/m) it was shown (that
is, compositions of the invention) that hydrocarbon
20 surfactants tested bring down the surface tension difference
closer to that of commercial product, also with HC 7801
styling resin.

- 31 -

WHAT IS CLAIMED IS:

1. An aqueous or hydroalcoholic hair styling aid
5 composition selected from the group consisting of:

10 I. an aqueous or hydroalcoholic non-aerosol hair styling aid composition comprising a water soluble or dispersable fixative polymer in an amount from 1% to 40 % by weight of the composition, a neutralizing agent in an amount from 0.1 to 10 wt%, a hydrocarbon based surfactant in an amount from 0.01% to 5% by weight, a salt from 0.01% to 10% by weight, alcohol from 0% to
15 90% by weight, and water from 10% to 98% by weight of the composition; and

20 II. an aqueous or hydroalcoholic aerosol hair styling aid composition containing a water soluble or dispersable fixative polymer in an amount from 1% to 40 % by weight of the composition, a neutralizing agent in an amount from 0.1 to 10 wt%, a hydrocarbon based surfactant in an amount from 0.01% to 5% by weight, a salt from 0.01% to
25 10% by weight, alcohol from 0% to 90% by weight, and water from 10% to 98% by weight of the composition and a liquified propellant gas from 5% to 60% by weight.

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- 33 -

sulfosuccinate or its acid form; magnesium dioctyl
sulfosuccinate or its acid form; ammonium dioctyl
sulfosuccinate or its acid form; sodium dodecyl
sulfate or its acid form; magnesium dodecyl sulfate or
5 its acid form; ammonium dodecyl sulfate or its acid
form; sodium laureth sulfate or its acid form;
magnesium laureth sulfate or its acid form; and
ammonium laureth sulfate or its acid form.

- 10 5. A composition according to claim 1 in which the
hydrocarbon surfactant is the zwitterionic surfactant
cocoamidopropyl betaine.
- 15 6. The composition according to claim 1 wherein the salt is
an organic salt selected from the group consisting of
sodium benzoate; magnesium benzoate; sodium acetate; and
magnesium acetate.
- 20 7. The composition according to claim 1 wherein the salt is
an inorganic salt selected from the group consisting of
sodium chloride and magnesium chloride.
- 25 8. The composition according to claim 1 wherein the alcohol
is selected from the group consisting of ethanol and
isopropanol.
9. A composition according to claim 1 which further
comprises silicone based surfactants in an amount from
0.01% to 5% by weight of the composition.

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- 35 -

17. A composition according to claim 1 which further comprises a volatile ester from about 10% to about 90% by weight.

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INTERNATIONAL SEARCH REPORT

Int. l. Application No

PCT/EP 00/01945

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>A. EACHUS ET AL.: "FORMULATING LOW-VOC HAIR SPRAYS FOR OPTIMUM PERFORMANCE" SOAP/COSMETICS/CHEMICAL SPECIALTIES, vol. 74, no. 9, 1998, pages 56-57, XP000915439 US the whole document</p>	1

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